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On the preparation of lecithin-stabilized oil-in-water emulsions by multi-stage premix membrane emulsification

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Abbreviated running title: Lecithin-stabilized O/W emulsion by membrane emulsification

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Abstract

We report on the preparation and characterization of lecithin-stabilized oil-in-water emulsions (10 or 20 wt% corn oil, 2 wt% lecithin, pH 3, 100 or 150 kPa) by multi-stage premix membrane emulsification using a *Shirasu porous glass* membrane (mean pore size 8 μm). Structural characteristics of the emulsions such as droplet size distribution, mean droplet diameter, and morphology were measured by using a laser light scattering and optical microscopy, respectively. As the number of passes through the membrane increased from 1 to 5, the transmembrane flux decreased from 30 to 1 $\text{m}^3\text{m}^{-2}\text{h}^{-1}$. It demonstrates that lecithin emulsifier, even if its net charge is negative ($\text{pK}_a \sim \text{pH } 1.5$), tends to foul SPG membrane by blocking the membrane pores, which was attributed to the possible interaction between positive groups on the lecithin molecules with anionic silanol groups on the membrane surface.

Keywords: Membrane emulsification; *Shirasu porous glass* membrane; Oil-in-water emulsion; Lecithin; Emulsion stability

1. Introduction

Food emulsions are usually prepared using high pressure homogenizers, ultrasound homogenizers or rotor/stator systems. The conventional emulsification devices generally use inhomogeneous extensional and shear forces and high energy inputs of 10^6 – 10^8 Jm⁻³ to rupture droplets (McClements, 2004). As a result, they generate emulsions with relatively small droplet sizes but wide droplet size distributions, and may cause loss of functional properties of shear and heat-sensitive components such as proteins, starches, DNA, etc. (Charcosset et al., 2004). Membrane emulsification (ME) is a relatively new emulsification technology employing low energy inputs of 10^4 – 10^6 Jm⁻³, developed for making emulsions with a controlled droplet size distribution over a wide range of mean droplet sizes ranging from less than 1 µm to more than 100 µm (Joscelyne & Trägårdh, 2000; McClements, 2004; Schubert & Engel, 2004; Vladislavljević & Williams, 2006). The two main types of ME processes have been developed; direct ME involving the permeation of pure dispersed phase through a microporous membrane into agitating or recirculating continuous phase and premix ME involving the passage of previously prepared coarse emulsion through the membrane (Charcosset et al., 2004). Premix ME provides several advantages over direct ME: (i) the optimal flux with regard to droplet uniformity is much higher (> 1 m³m⁻²h⁻¹ vs 0.001 – 0.1 m³m⁻²h⁻¹); (ii) the mean droplet sizes are smaller; (iii) the experimental setup is simpler and easier to operate; (iv) the process parameters are easier to control than in direct ME. One of the disadvantages of premix ME is a higher emulsion polydispersity compared with direct ME (Charcosset et al., 2004; Joscelyne & Trägårdh, 2000). However, the monodispersity can be improved by increasing the number of homogenization cycles and this mode of operation is known

as the multi-stage (repeated) premix ME or repeated membrane homogenization (Charcosset et al., 2004; Vladisavljević et al., 2006a). Some examples of investigations on membrane homogenization carried out by different research groups are summarized in Table 1. The resultant emulsion droplets are often used as templates for production of solid microparticles, such as polylactide microspheres (Sawalha et al., 2008) and solid lipid microspheres (Vladisavljević & Williams, 2005).

The most commonly used membrane for the preparation of emulsion is the *Shirasu porous glass* (SPG) membrane (Vladisavljević et al., 2007). The SPG membrane is inherently hydrophilic (thus suitable for O/W emulsions preparation) due to the presence of negatively charged silanol groups on the surface (Vladisavljević et al., 2005). For the success of ME using SPG, a chosen emulsifier should not adsorb to the membrane surface by electrostatic or hydrophobic interactions because it can cause the alteration of membrane polarity from hydrophilic to hydrophobic or vice versa, and it should not accumulate inside the pores, which can lead to the pore plugging. Here, lecithin was selected as an emulsifier in multi-stage premix ME using SPG membrane because it is a negatively charged food grade emulsifier widely used in the food industry and can produce small oil droplets during conventional homogenization processes. It is a naturally occurring surface-active molecule that can be extracted from a variety of sources such as soybeans, rapeseed, and egg (Stauffer, 1999). In addition, it can be totally biodegraded and metabolized thus virtually non-toxic.

Therefore, the aim of this work is to determine whether lecithin-stabilized O/W emulsions with uniform droplets and narrow droplet size distribution could be created by the multi-stage premix ME using hydrophilic SPG membrane. To investigate the

production of O/W emulsions, the transmembrane flux, mean droplet diameter, and morphology of the emulsions were examined after each membrane pass. It is important to note that lecithin has not been used as an emulsifier in any membrane homogenization study reported so far, including those listed in Table 1.

2. Materials and methods

2.1. Materials

Lecithins were kindly provided from Archer Daniels Midland Company (ULTRALEC, Decatur, IL, USA). As stated by the manufacturer, the lecithin powders are manufactured by a new ultrafiltration process from soy phospholipids, and consist primarily of phosphatidylcholine, phosphatidylethanolamine, and phosphatidylinositol, as shown in Fig. 1. Analytical grade sodium azide (NaN_3), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were purchased from the Sigma Chemical Company (St. Louis, MO, USA). Corn oil was purchased from a local supermarket and used without further purification. Distilled and deionized water was used for the preparation of all solutions.

2.2. Preparation of solutions and emulsions

A buffer solution was prepared by dispersing 100 mM acetic acid and 0.02 wt% NaN_3 (as an antibacterial agent) in water and then adjusting the pH to 3.0. An emulsifier solution was prepared by dispersing 2.0 wt% lecithin into the buffer solution. The emulsifier solution was sonicated for 1 min at a frequency of 20 kHz, amplitude of 70%, and duty cycle of 0.5 s (Model 500, sonic dismembrator, Fisher Scientific, Pittsburgh, PA,

USA) to disperse the emulsifier. The pH of the solution was adjusted to 3.0 by use of HCl and/or NaOH, and then the solution was stirred for about 1 hr to ensure complete dispersion of the emulsifier.

Oil-in-water emulsions (emulsion 1: 20 wt% corn oil, 1.6 wt% lecithin, produced at 100 kPa; emulsion 2: 10 wt% corn oil, 1.8 wt% lecithin, produced at 150 kPa) were prepared by homogenizing corn oil and the aqueous lecithin solution using membrane homogenization apparatus (Fig. 2A). The oil and lecithin solution were first premixed for several minutes using a stirring bar followed by five passes through a membrane homogenizer at 100 or 150 kPa (External pressure-type micro kit, MG-20-5, Kiyomoto Iron Works Ltd., Japan). The pressure vessel was filled with 100 mL of the premix, and the required driving pressure was built up with compressed air using a precision pressure regulator (PRG101, Omega, Stamford, CT, USA). The operating pressure was measured with an accuracy of ± 1 kPa using a digital pressure gauge (PG-200-103G-P, Copal Electronics, Tokyo, Japan). The emulsion that had passed through the membrane tube from outside to inside was collected into a beaker placed on an electronic balance (Accu-622, Fisher Scientific, Fair Lawn, NJ, USA). The balance was interfaced to a personal computer to record time and mass data every 2 s using an installed data acquisition software (AccuSeries USB version 1.2, Fisher Scientific, Fair Lawn, NJ, USA); these data were used to calculate the transmembrane flux for each passage of the emulsion through the membrane. The experiments were carried out at 19.7 °C. The membrane used in this study was a SPG membrane (8.5 mm inner diameter $\times$ 0.8 mm wall thickness) supplied from SPG Technology Co., Ltd. (Sadowara, Japan). The microstructure of the membrane examined by Scanning Electron Microscopy (SEM) and high resolution x-ray

microtomography (XMT) is shown in Fig. 2B. The mean pore size of the membrane was 8.0 μm , the effective membrane length was 12 mm, and the effective cross-sectional area was 3.75 cm^2 . The membrane was cleaned after use by immersing it for 2 days in ethanol plus 2 days in toluene, followed by heating at 500 $^{\circ}\text{C}$ for 30 min in an electric muffle furnace. Measurements of the pure water flux after cleaning indicated that the inherent membrane permeability to pure water was completely restored by this treatment.

The emulsion samples were collected after each membrane cycle and then analyzed for their droplet size, droplet size distribution, and microstructure within 3 h after preparation.

2.3. Droplet size determination

To avoid multiple scattering effects, emulsions were diluted to a droplet concentration of approximately ~0.005 wt% using buffer solution at the pH of the sample and stirred continuously throughout the measurements to ensure the samples were homogenous. The droplet size distribution of the emulsions was then measured using a laser light scattering instrument (Mastersizer MSS, Malvern Instruments, Worcestershire, UK). This instrument measures the angular dependence of the intensity of laser light ($\lambda = 632.8 \text{ nm}$) scattered by a dilute emulsion, and then finds the droplet size distribution that gives the best fit between experimental measurements and predictions based on light scattering theory. The mean droplet size was reported as the surface-weighted mean diameter, d_{32} ($=\sum n_i d_i^3 / \sum n_i d_i^2$) or the volume-weighted mean diameter, d_{43} ($=\sum n_i d_i^4 / \sum n_i d_i^3$), where n_i is the number of droplets in the i -th range of sizes, the mean diameter of which is d_i . The d_{43} value is more sensitive to the presence of large droplets than the d_{32} value, and therefore

it can give a good indication of droplet aggregation. All measurements were carried out for two freshly-prepared samples and results are reported as averages.

2.4. Optical microscopy

Emulsions were gently agitated in a glass test tube before analysis to ensure that they were homogenous. A drop of emulsion was placed on a microscope slide and then covered with a cover slip. The microstructure of the emulsion was then observed using conventional optical microscopy (Nikon microscope Eclipse E400, Nikon Corporation, Japan). The images were acquired using a CCD camera (CCD-300T-RC, DAGE-MTI, Michigan City, IN) connected to Digital Image Processing Software (Micro Video Instruments Inc., Avon, MA) installed on a computer.

3. Result and discussion

3.1. Transmembrane flux of lecithin-stabilized O/W emulsions

Typically, in premix membrane emulsification (ME), transmembrane flux tends to increase with increasing the number of emulsification cycles, as shown in Fig. 3. It can be explained by the fact that droplet size tends to reduce as the number of cycles increases, thus usually lesser energy is needed to push the droplets through the membrane pores. The role of transmembrane pressure is to provide a driving force for emulsion flow through the membrane pores and to effect the breakup of drops (Vladislavljević et al., 2006):

$$\Delta p_{tm} = \underbrace{\eta_{pore}(R_m + R_{f,i})J_i}_{\Delta p_{flow}} + \underbrace{C\phi\gamma(1/d_i - 1/d_{i-1})}_{\Delta p_{break}} \quad (1)$$

where C is a constant, ϕ is the volume fraction of dispersed phase in the emulsion, γ is the interfacial tension, η_{pore} is the emulsion viscosity in the pores, J_i and d_i are the transmembrane flux and the final mean particle size of the i th pass, R_m is the hydraulic resistance of a clean membrane, and $R_{f,i}$ is the overall fouling resistance for the i th pass. The fouling resistance is a consequence of the accumulation of oil phase and the solutes in the continuous phase on the membrane surface and inside the pores. The increase in flux, J_i , typically observed in constant-pressure membrane homogenization (Fig. 3) can be explained by a decrease in Δp_{break} , due to d_i tending to a constant limiting value. The limiting flux in Fig. 4 corresponds to $d_i = \text{const}$ and $\Delta p_{break} = 0$. The higher limiting flux at the lower dispersed phase content (10 wt.%) can be explained by the fact that η_{pore} increases with increasing the dispersed phase content and accordingly, J_i decreases in repeated passes at $\Delta p_{tm} = \text{const}$.

However, for the lecithin-stabilized emulsion, the highest transmembrane flux was observed at the first pass and obviously the flux decreased with increasing the number of passes (Fig. 4). There are several possible reasons to account for this observation. Firstly, the fraction of dispersed oil droplet phase in lecithin-stabilized O/W emulsions was relatively high. Emulsions with high dispersed phase fractions cannot pass through the membrane easily because the disruption of large number of droplets requires large amounts of mechanical energy, resulting in a low transmembrane flux. As predicted from Eq. (1), the higher amount of energy used for droplet break-up, the lower energy amount remaining for emulsion flow. Secondly, the applied pressure was not high enough to effectively push the emulsion droplets through the membrane pores. The above two factors should facilitate plugging the membrane pores, however this problem could be overcome by adjusting the operating parameters (Ribeiro et al., 2005; Vladisavljević et al., 2004). Thirdly, the lecithin molecules cannot easily pass through the membrane due to very tortuous pores and relatively thick membrane wall, thus the macromolecules were accumulated within the membrane and thus transmembrane flux decreased in repeated passes. Lastly, a membrane fouling occurred due to the attractive electrostatic interaction between the positive patches (e.g. $-\text{N}(\text{CH}_3)_3^+$ or $-\text{NH}_3^+$) on the lecithin molecules (such as zwitterionic phosphatidylcholin and phosphotidyletanolamine) and the anionic silanol groups ($-\text{Si}-\text{O}^-$) on the SPG membrane, although the net electrical charge of the emulsion droplets coated by lecithin was negative at pH 3 (Ogawa et al., 2003, 2004; Stauffer, 1999). According to Israelachvili (1992) and Ogawa et al. (2004), the pK_a value of the anionic phosphate groups on lecithins are typically around pH 1.5. As a result of this electrostatic interaction, the membrane surfaces and/or pores became progressively

blocked by the lecithin molecules and/or the emulsion droplets, due to which mechanism the maximum flux was observed in the first pass corresponding to a minimum fouling resistance. The last two possible reasons for the unusual J vs n relationship (Fig. 4) are due to the inherent physicochemical properties of SPG membrane.

Initially, we prepared and characterized only the lecithin-stabilized O/W emulsions consisting of 20 wt% corn oil and 80 wt% aqueous phase at a pressure of 100 kPa (emulsion 1). Then, we aimed to determine if the transmembrane flux could be sufficiently increased by decreasing the dispersed phase fraction and increasing the pressure, thus lecithin-stabilized O/W emulsions containing 10 wt% corn oil were prepared at 150 kPa (emulsion 2). The two parameter values were selected based on the previous work conducted by Vladisavljević et al. (2004) using Tween 80-stabilized multiple emulsion droplets, where flux in the first pass increased by a factor of 4 as a result of the same variation of experimental conditions. Fig. 4 shows that appreciably higher flux was reached in the first cycle by a combination of higher pressure and lower dispersed phase fraction than that of emulsion 1, however the flux tended to diminish abruptly as the number of cycle increased and eventually its increase was negligible after five passes. It suggests that the changes in the critical process parameters controlling transmembrane flux did not prevent the membrane pores from being plugged in multi-stage premix ME for the preparation of lecithin-stabilized O/W emulsions.

3.2. Structural characteristics of the lecithin-stabilized O/W emulsions

The lecithin-stabilized O/W emulsions produced by multi-stage premix ME were examined for their mean droplet diameters (Fig. 5), droplet size distributions (Fig. 6), and morphologies (Fig. 7).

Typically, the droplets of a pre-emulsion are disrupted into smaller droplets during their permeation through the membrane in premix ME (Charcosset et al., 2004). For the two emulsions prepared, the volume-surface mean droplet diameter (d_{32} , which is more sensitive to the presence of small droplets) and the volume-weighted mean droplet diameter (d_{43} , which is more sensitive to the presence of large droplets) were very large, although both d_{32} and d_{43} tended to decrease with increasing the number of passes (Fig. 5). Until the second pass, the droplet size distributions of both emulsions were mono-modal with a peak corresponding to considerably large droplets, then turned to either bimodal or multi-modal consisting of a major peak corresponding to large droplets and minor peaks corresponding to small fractions of relatively small droplets in successive cycles. With increasing the number of passes, the major peak tended to shift, though not appreciably, to smaller droplet diameters and a minor peak was arising around the membrane pore size of 8 μm (Fig. 6). Optical microscopy measurements indicated that large emulsion droplets ($d > 50 \mu\text{m}$) were present in all lecithin-stabilized emulsions regardless of processing conditions and number of membrane passes, although the droplets became definitely smaller and more uniform when the homogenization was repeated (Fig. 7). The presence of large droplets could be a consequence of droplet re-coalescence. However, we believe that re-coalescence was negligible in our experiments, because balance between droplet disruption and re-coalescence depends on the energy input during

emulsification (Jafari et al., 2008) and the energy input in membrane homogenization is normally 3 to 4 orders of magnitude lower than in high-energy homogenization methods, such as high-shear homogenization with high-pressure or rotor-stator systems. For example, the transmembrane pressures in these experiments were 100-150 kPa, whereas in Microfluidizers and Jet Dispersers the homogenizing pressures could be as high as 700 MPa (Jafari et al., 2008).

The emulsions 2 (10 wt% oil, 150 kPa) prepared with the lower dispersed fraction at higher pressure had relatively smaller droplets compared with emulsions 1 (20 wt% oil, 100 kPa) (Fig. 5–7). It could be attributed to the fact that droplets pass through the membrane more quickly and thus are disrupted more easily into smaller droplets during the permeation at lower concentration and higher pressure. In addition, the droplets in emulsions 2 have less opportunity to interact with other droplets due to lower droplet concentration (Charcosset et al., 2004; Joscelyne & Trägårdh, 2000; Ribeiro et al., 2005; Vladisavljević & Schubert, 2003; Vladisavljević et al., 2004).

Overall, the changes in the critical parameters such as dispersed phase content and pressure during the emulsion preparation did not appreciably improve the structures of the lecithin-stabilized O/W emulsions by ME using SPG membrane. It suggests that the adequate choice of emulsifier is of primary importance for the success of ME, i.e., a chosen emulsifier for the ME using SPG membranes must not carry charge opposite to that of the membrane surface, regardless of its net electrical charge.

4. Conclusions

The objective of this study was to determine whether lecithin-stabilized O/W emulsions could be created by the multi-stage premix ME using hydrophilic SPG membrane. The experiments reported here have demonstrated that lecithin emulsifier, in spite of its net charge is negative ($pK_a \sim \text{pH } 1.5$), tended to foul SPG membrane by blocking the membrane pores because the positive groups on the lecithin molecules could interact with anionic silanol groups on the SPG surface, and that there were large populations of relatively large oil droplets ($d > 50 \mu\text{m} \approx >50 \text{ vol\%}$) in all lecithin-stabilized emulsions. Nevertheless, it was found that droplet diameters in the lecithin-stabilized O/W emulsions tended to decrease with increasing the number of membrane cycles. The finding of this study may provide practical information on the requirements and the properties of emulsifiers for preparing stable O/W emulsions by repeated ME using SPG membrane.

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Table 1. Examples of premix membrane emulsification studies

Membrane material	System	Mean pore size, d_m (μm)	Product emulsion	Mean droplet size and span	Flux ($\text{m}^3 \text{m}^{-2} \text{h}^{-1}$)	Authors
Tubular SPG	Cross flow	2.7 and 4.2	O/W	$(1.4-2.1) \times d_m$, span = 0.4-0.62	0.03-3.5	Suzuki et al. (1996)
Flat PTFE	Dead end	1.0	O/W and W/O	$(2-4.1) \times d_m$	Up to 9	Suzuki et al. (1998)
Flat PTFE	Dead end with phase inversion	1.0	O/W and W/O	$(2.8-4.0) \times d_m$	1-5.5	Suzuki et al. (1998)
Flat PTFE	Dead end, multi-stage (n=1-3)	1.0	O/W	$(1.2-2.6) \times d_m$ Span = 0.55-0.9	2-18	Altenbach-Rehm et al. (2002)
Flat cellulose acetate	Dead end	0.2, 0.45, 0.8 and 3.0	W/O/W	$(1.0-3.5) \times d_m$	Not specified	Shima et al. (2004)
Flat polycarbonate	Dead end, multi-stage (n=1-18)	0.33, 0.38, 0.44, 0.6 and 1.0	O/W	$\leq 1.6 \times d_m$ for n > 12	0.2-0.6	Park et al. (2001)
Tubular SPG	Dead end multi-stage (n=3)	1.1	S/O/W	$0.9 \times d_m$	1.6	Toorisaka et al. (2003)
Tubular SPG	Dead end, multi-stage (n=1-5)	10.7	W/O/W	$(0.41-1.2) \times d_m$ span=0.28-0.6	0.8-37	Vladislavljević et al. (2004)
Tubular SPG	Dead end, multi-stage (n=1-5)	5.4-20.3	O/W and W/O/W	$(0.37-1.2) \times d_m$ span = 0.28-0.93	2-240	Vladislavljević et al. (2006a)
Tubular SPG	Dead end, multi-stage (n=1-5)	8.0	O/W	$(0.5-1.4) \times d_m$ and span = 0.33-0.77 at n = 5	3-60	Vladislavljević et al. (2006b)
Tubular SPG	Dead end, multi-stage (n=5)	8.0	W/O/W	$(0.20-0.29) \times d_m$	70 at n=5	Surh et al. (2007)
Tubular α -alumina	Stirring	1.5	O/W	$(1.5-1.8) \times d_m$ span = 1-1.2	0.42-0.62	Jing et al. (2005)
Flat polycarbonate	Dead end, multi-stage (n=5)	-	W/O/W	0.7-2.5 μm	3.7-14.7	Yafei et al. (2006)
Glass filter	Dead end, multi stage (n=11)	1.0	O/W	-	-	Sawalha et al. (2008)

Figure Captions

Fig. 1. Structures of major chemicals contained in the crude lecithin powders used in this study. The lecithin powders from soy phospholipids consist primarily of phosphatidylcholine, phosphatidylethanolamine, and phosphatidylinositol. R_1 and R_2 in the structures represent fatty acids.

Fig. 2. Schematic diagram of the membrane homogenization apparatus (A) and typical SEM and XTM images of *Shirasu porous glass* (SPG) membrane (B). The pictures were cited from our previous works (Vladislavljević et al., 2006b; 2007) to help readers' understanding. Fig. 2B clearly shows that SPG membrane consists of interconnected pores with irregular cross sections.

Fig. 3. Typical relationships between transmembrane flux and number of repeated passes for constant-pressure membrane homogenization in the absence of membrane fouling.

Fig. 4. Variation of transmembrane flux with number of passes through the membrane homogenizer for O/W emulsions stabilized by lecithin (2.0 wt% lecithin dispersed into 100 mM acetate buffer at pH 3).

Fig. 5. Influence of the number of passes through the membrane homogenizer on mean droplet diameters d_{32} (A) and d_{43} (B) of O/W emulsion stabilized by lecithin. Emulsifier solution was prepared by dispersing 2.0 wt% lecithin into 100 mM acetate buffer at pH 3. Two kinds of emulsions were prepared: the emulsions 1 consisting of 20 wt% corn oil and 80 wt% emulsifier solution and the emulsions 2 consisting of 10 wt% corn oil and 90 wt% emulsifier solution were produced at 100 kPa and 150 kPa, respectively.

Fig. 6. Influence of the number of passes through the membrane homogenizer on droplet size distribution of O/W emulsion stabilized by lecithin. Please see legend of Fig. 4 for details on the emulsions.

Fig. 7. Photomicrographs of O/W emulsions stabilized by lecithin (20 wt% corn oil, 1.6 wt% lecithin, produced at 100 kPa or 10 wt% corn oil, 1.8 wt% lecithin, produced at 150 kPa). More than 6 pictures were taken per each emulsion and a representative one was presented.

Phosphatidylcholine

Phosphatidylethanolamine

Phosphatidylinositol

Fig. 1. Surh et al.

A

300 μm

B

Fig. 2. Surh et al.

Fig. 3. Surh et al.

Fig. 4. Surh et al.

Fig. 5. Surh et al.

Fig. 6. Surh et al.

Fig. 7. Surh et al.